

## **PRELIMINARY ROUND-ROBIN STUDIES ON THE ICTAC CERTIFIED REFERENCE MATERIALS FOR DTA Barium carbonate and strontium carbonate**

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The ICTAC Committee on Standardisation has formed a Task Group to investigate the suitability of the ICTAC Certified Reference Materials for DTA, covering the temperature range 450°–1100°C, for accurate temperature calibration purposes and to evaluate their potential as enthalpy calibrants for DTA and DSC equipment. This paper reports the results of preliminary round-robin studies on barium carbonate and strontium carbonate, using a dual-point calibration method based on the melting points of aluminium and gold. In addition the fusion of ICTAC potassium sulphate has been investigated as a possible calibration transition.

**Keywords:** barium carbonate, DTA, dual-point calibration method, reference materials, strontium carbonate

### **Introduction**

The Committee on Standardisation of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) is responsible for a wide range of Certified Reference Materials (CRMs) for the temperature calibration of thermal analysis equipment [1]. The CRMs were primarily developed for use as inter-laboratory comparison materials and are distributed by the U.S. National Institute for Standards and Technology.

The ICTAC Committee on Standardisation has formed a series of Task Groups to investigate the suitability of the present materials for accurate temperature calibration. This paper presents some preliminary work carried out by the Task Group concerned with the CRMs for DTA covering the temperature range 450°–1100°C. In addition to evaluating the current materials for accurate temperature calibration purposes, their potential as enthalpy calibrants for DTA and DSC

equipment was also to be investigated by determining reproducibility of the peak area measurements.

Preliminary studies on ICTAC potassium chromate, carried out by a U.K. Working Group have shown considerable promise and a mean value for the extrapolated onset temperature of  $669.1 \pm 0.2^\circ\text{C}$  was obtained from three laboratories using a total of six instruments [2].

In the present work programme, preliminary round-robin studies have been carried out on ICTAC barium carbonate and strontium carbonate. A dual-point calibration method was adopted using the melting points of aluminium and gold. In addition, the possibility of using the melting point of ICTAC potassium sulphate, at approximately  $1070^\circ\text{C}$ , for temperature calibration purposes was also investigated.

## Experimental

The following instruments were used in the test programme

Netzsch DSC 404

Perkin Elmer DTA 1700

Seiko DSC 320

Stanton Redcroft STA 1500

Participants were asked to carry out a two-point calibration of their apparatus according to the ASTM Method E 967-83 [3]. The calibration materials, supplied in the form of 0.5 mm diameter wires, were aluminium (Goodfellow Metals 99.999% purity) and gold (Goodfellow Metals 99.99+% purity). Values for the melting points of aluminium ( $660.32^\circ\text{C}$ ) and gold ( $1064.18^\circ\text{C}$ ) were taken from the International Temperature Scale of 1990 (ITS-90) [4].

While alumina crucibles were specified for the calibration experiments, in order to avoid possible interaction between alumina and barium and strontium carbonates at high temperatures, platinum crucibles were used for the experiments on these materials. To evaluate the magnitude of the temperature correction between the two crucible materials, additional experiments were carried out in both crucible types using the solid–solid phase change of ICTAC potassium chromate and fusion of ICTAC potassium sulphate. Measurements on the latter material enabled the suitability of this transition for accurate temperature calibration purposes to be evaluated and an estimate of the transition temperature to be made by direct comparison with the melting point of gold.

Suggested sample weights were 20 mg for the ICTAC materials, 10 mg for aluminium and 50 mg for gold. The powder samples were to be lightly tamped into crucibles and covered with loose fitting lids. A heating rate of  $3^\circ\text{C}\cdot\text{min}^{-1}$  was specified and the experiments had to start at least  $50^\circ\text{C}$  below the transition temperature. Duplicate experiments were to be carried out on two samples of each material, except for potassium sulphate where a single experiment was

specified in order to reduce the effects of the molten material creeping after fusion. In order to obtain smooth well-defined peaks it was recommended that aluminium and gold were pre-melted before making the measurements. The atmosphere specified was dry high-purity nitrogen at the flow rate normally used. Participants were asked to measure the extrapolated onset temperatures of the transitions to 0.1°C and also to measure the DTA/DSC peak areas.

**Table 1** Precision of the calibration experiments for aluminium and gold

Laboratory	Temperature precision/°C	
	Aluminium	Gold
A	0.2	0.5*
B	0.1	0.0
C	0.1	0.8
D	0.2	0.4

\*Instrument reads to 1° above 1000°C.

## Results and discussion

The errors associated with the calibration experiments using aluminium and gold are shown in Table 1. In the case of laboratory A the instrument software only allowed measurements to be made to the nearest 1°C above 1000°C, producing an uncertainty of  $\pm 0.5^\circ\text{C}$  in the result for gold.

Comparison of the uncorrected results obtained for potassium chromate and potassium sulphate in both alumina and platinum crucibles is shown in Table 2. Apart from Laboratory D, where a platinum liner inside an alumina crucible was used in place of a platinum crucible, the results obtained were similar for both crucible materials, indicating that the calibration results can be applied directly without additional corrections.

**Table 2** Extrapolated onset temperatures for transitions in potassium chromate and potassium sulphate measured in alumina and platinum crucibles (uncorrected data)

Laboratory	Extrapolated onset temperature/°C			
	K <sub>2</sub> CrO <sub>4</sub>		K <sub>2</sub> SO <sub>4</sub>	
	Al <sub>2</sub> O <sub>3</sub>	Pt	Al <sub>2</sub> O <sub>3</sub>	Pt
A	669.7 $\pm$ 0.0	669.6 $\pm$ 0.0	1070.5 $\pm$ 0.5	1070.4 $\pm$ 0.5
B	672.0 $\pm$ 0.1	672.2 $\pm$ 0.1	1071.3 $\pm$ 0.2	1071.2 $\pm$ 0.1
C	671.9 $\pm$ 0.3	672.3 $\pm$ 0.1	1075.4 $\pm$ 0.5	1075.0 $\pm$ 0.2
D	668.5 $\pm$ 0.4	669.5 $\pm$ 0.2	1067.7 $\pm$ 0.1	1069.6 $\pm$ 0.3

Laboratory A – instrument reads to 1°C above 1000°C

Laboratory D used Pt liners inside alumina crucibles

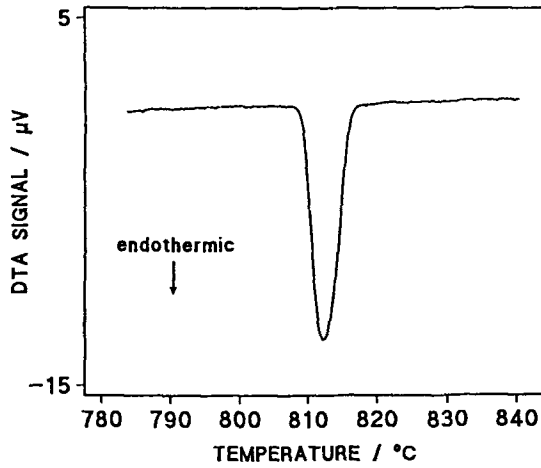


Fig. 1 DTA curve for ICTAC barium carbonate (sample weight, 20.2 mg; heating rate,  $3^{\circ}\text{C}\cdot\text{min}^{-1}$ ; atmosphere, nitrogen)

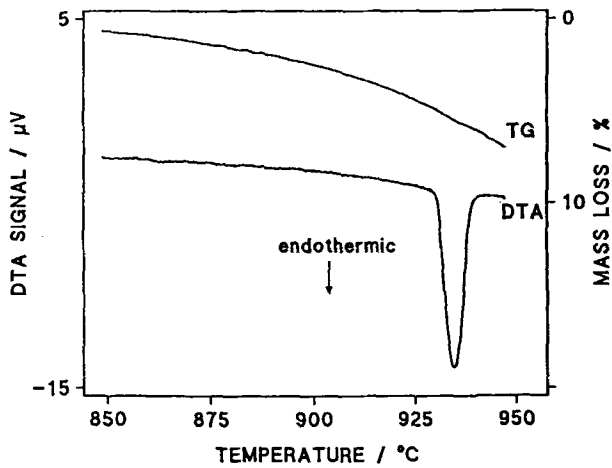


Fig. 2 Simultaneous TG-DTA curve for ICTAC strontium carbonate (sample weight, 19.7 mg; heating rate,  $3^{\circ}\text{C}\cdot\text{min}^{-1}$ ; atmosphere, nitrogen)

Typical DTA curves for solid–solid transitions of barium carbonate and strontium carbonate and the fusion of potassium sulphate are shown in Figs 1–3. In the last case the curve for gold has been included for comparison, and the TG curve is also shown for the strontium salt.

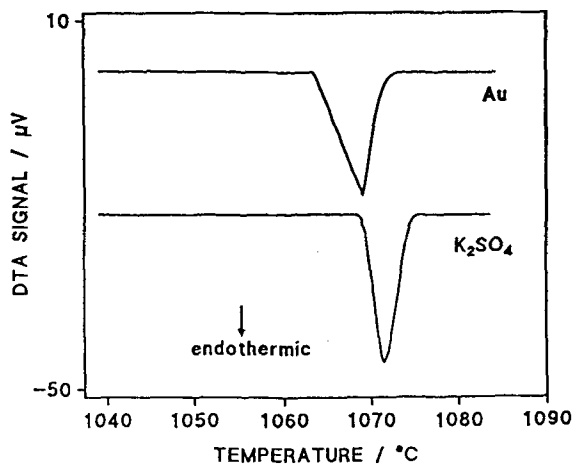


Fig. 3 DTA curves for ICTAC potassium sulphate (20.1 mg) and for gold (49.9 mg) (heating rate  $3^{\circ}\text{C}\cdot\text{min}^{-1}$ ; atmosphere, nitrogen)

Although the ICTAC Certificates recommend that only a single heating experiment is carried out on a given sample, it is common practice to carry out at least duplicate experiments on a single sample. The validity of this approach for the materials used in the current programme is demonstrated in Table 3. The results indicated that apart from barium and strontium carbonates, there was no significant difference between the two measurements.

Table 3 Difference in extrapolated onset temperatures for 1st and 2nd heating experiments

Laboratory	Temperature difference/ $^{\circ}\text{C}$				
	Al	K <sub>2</sub> CrO <sub>4</sub>	BaCO <sub>3</sub>	SrCO <sub>3</sub>	Au
A	0.0	-0.2	0.3	5.2	1
	-0.3	0.0	1.1	5.5	0
B	0.1	0.0	0.8	5.7	0.0
	-0.1	0.0	1.2	6.1	0.4
C	-0.1	0.2	0.8	-	0.2
	0.0	-0.2	0.6	-	0.1
D	0.3	0.1	0.8	2.9	-
	-0.3	0.4	0.4	4.0	0.2

For barium carbonate, marked sintering of the sample was found to take place over the transition region, resulting in the formation of a cylindrical pellet. This shrinkage was also observed during measurements to evaluate the suitability of

the ICTAC CRMs for DTA for the temperature calibration of thermomechanical analysers [5]. If the pellet was crushed before the second experiment, the result obtained was similar to that for the first experiment, indicating that the increase in the measured temperature was due to heat transfer effects.

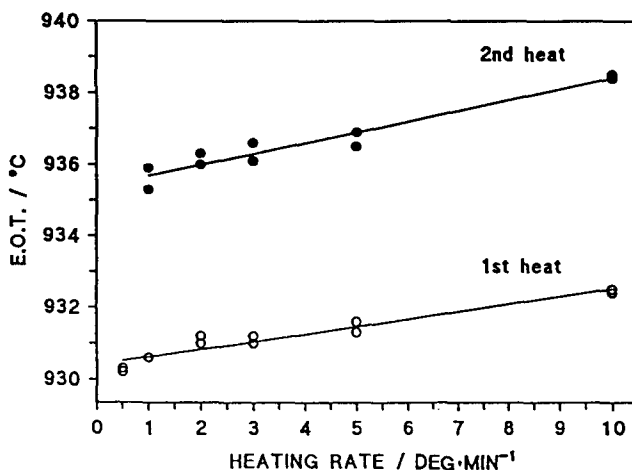


Fig. 4 Plots showing the influence of heating rate on the transition temperature of strontium carbonate

For strontium carbonate, the temperature difference between the first and second experiments on a given sample was of the order of 5°C. For this material, although some sintering had also occurred, it can be seen from Fig. 2 that thermal decomposition was also taking place in the transition region. A second experiment on a sample will therefore be performed on partially decomposed material. It can be seen however from Fig. 4, which shows the effect of heating rate on the transition temperature for the first and second heating experiments, that the increase in transition temperature is not directly related to the extent of decomposition, which is much higher at the slower heating rates.

The corrected extrapolated onset temperatures, based on the first heating experiment for each sample, for the transitions in barium and strontium carbonates and potassium sulphate are given in Table 4. Although results for the carbonates do not show the very close inter-laboratory agreement obtained for potassium chromate, they are sufficiently encouraging to warrant further investigation of these materials as high-temperature calibration standards.

Agreement in the values for melting temperature of potassium sulphate is very good and suggests the possibility of using this material for two-point temperature calibrations (the use of this material as an ICTAC CRM is based on the solid-solid phase transition in the region of 585°C). Only one laboratory experienced

problems due to creep of the liquid melt and this may have been due to minute cracks in the crucible walls.

**Table 4** Corrected values for extrapolated onset temperatures measured for barium carbonate, strontium carbonate and potassium sulphate

Laboratory	Extrapolated onset temperature/°C		
	BaCO <sub>3</sub>	SrCO <sub>3</sub>	K <sub>2</sub> SO <sub>4</sub>
A	807.3±0.3	930.9±0.1	1070.2±0.5
B	808.1±0.1	930.7±0.1	1070.1±0.2
C	810.8±0.3	931.9±0.5	1070.0±0.5
D	809.2±0.3	932.5±1.1	1070.0±0.4
Mean	808.8±1.4	931.4±0.8*	1070.1±0.4

\*One value from Laboratory *D* omitted.

It is clear from the results reported previously for potassium chromate and the current measurements on potassium sulphate that good inter-laboratory agreement is given when the sample being measured has a transition temperature close to that of one of the calibration materials. This would suggest that the inter-laboratory variations in the values for the carbonates may be due to non-linearity in the temperature dependence of the temperature correction.

From the results supplied by two of the participating laboratories, peak area measurements on barium carbonate and potassium sulphate showed good reproducibility and in all cases results were repeatable to better than 2%. There appeared to be no significant difference between the peak areas in the first and second experiments on barium carbonate.

Both materials are therefore worthy of consideration as enthalpy standards. Since strontium carbonate is decomposing in the region of the phase transition, this material is not suitable as an enthalpy calibrant.

## Conclusions

Preliminary round-robin studies on ICTAC barium carbonate and strontium carbonate have produced mean values of 808.8±1.4°C and 931 ±0.8°C respectively for the extrapolated onset temperatures. Both materials are recommended for only a single heating experiment. Further work is required before the materials are submitted for studies by high-temperature calorimetry.

Good reproducibility has been obtained for the melting temperature of potassium sulphate and this material offers considerable promise as a dual-point temperature calibrant covering the range 580°–1070°C.

Peak area measurements on barium carbonate and potassium sulphate showed good precision and indicate that these materials may be considered as potential enthalpy standards.

## References

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**Zusammenfassung** — Der ICTAC Committee on Standardisation bildete eine Arbeitsgruppe zur Untersuchung der Eignung ICTAC-zertifizierter DTA-Referenzsubstanzen im Temperaturbereich 450°–1100°C für präzise Temperaturkalibrierung und zur Auswertung deren Einsatzmöglichkeit als Enthalpiekalibriermaterialien für DTA- und DSC-Apparaturen. Vorliegend wird über die Ergebnisse von Vorstudien an Bariumcarbonat und Strontiumcarbonat berichtet, wobei eine Zweikalibrierpunktmethode verwendet wurde, die auf den Schmelzpunkten von Aluminium und Gold beruht. Zusätzlich wurde das Schmelzen von ICTAC Kaliumsulfat als mögliche Kalibrierungsumwandlung untersucht.